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Reactions of antioxidants with molecular oxygen. Part I. 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) in silicone matrix

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ABSTRACT

The reaction of 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) stabiliser with oxygen was studied in an inert substrate at 80–120 °C temperature under 0.02–3.0 MPa oxygen pressure ranges. UV/VIS spectrophotometry and Gel Permeation Chromatography were used to follow the antioxidant consumption and the formation of oxidation products. A simplified mechanistic model of stabiliser oxidative transformation was proposed and corresponding kinetic parameters were determined and compared with the kinetic values obtained by other authors.

Keywords:

Phenolic antioxidant

Thermal oxidation

Kinetics

UV/VIS

GPC

1. Introduction

Antioxidants are widely used in industry to slow down the deterioration of polymer properties resulting from polymer oxidation and thus to extend the material's lifetime. Hindered phenolic stabilisers are commonly used as effective antioxidants. Stabilisation mechanisms can be relatively complex. There is a wide consensus on the mechanism of the primary step, but various secondary processes can occur and their relative importance is not very clear. A part of the stabiliser interacts with polymer transformation products, whereas another part of the stabiliser can be lost by physical migration out of the polymer or direct interaction with molecular oxygen [1]. The direct reaction of antioxidant with oxygen has been discussed in several articles [2–4]. In the case of phenolic antioxidants, the hydrogen atom of the hydroxyl group can be removed by direct attack of oxygen, which generates phenoxyl radicals. These radicals are able to initiate a complex reaction series and subsequently yield numerous transformation products. The contribution of the direct reaction between the hydroxyl group of antioxidant and oxygen can be important, especially in the case of accelerated aging at high temperatures and under high oxygen pressures. It can be reasonably assumed that the oxygen–phenol

reaction and the peroxy–phenol reaction (the main stabilisation event) have many common features, especially side reactions. Therefore, knowledge of these processes and especially their contribution in the overall process is crucial for lifetime prediction and related kinetic modelling.

Although the reaction with oxygen has proposed a long time ago, literature giving the corresponding kinetic parameters is relatively scarce. Various authors [5–8] have performed this study using a polymer matrix. However, a better understanding of the problem could be achieved if the reaction was studied in an inert substrate, removing the interference of other existing reactions between the antioxidant and peroxy or alkyl macroradicals.

The aim of the present study is to determine kinetic parameters of the reaction of 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) stabiliser with oxygen. These parameters are necessary for the kinetic modelling of the oxidation of stabilised polymers. The analysis was carried out in an inert substrate to avoid the reactions involved during the thermal oxidation of an oxidisable substrate. Silicone oil is suggested as an inert substrate, which presents a number of advantages such as: a negligible physical loss and its direct use in the analytical techniques without a previous preparation. A wide range of experimental conditions was investigated to obtain the accurate values. The stabiliser depletion and transformation products were monitored by two different techniques: UV/VIS spectrophotometry and Gel Permeation Chromatography. Both techniques were compared and tested.

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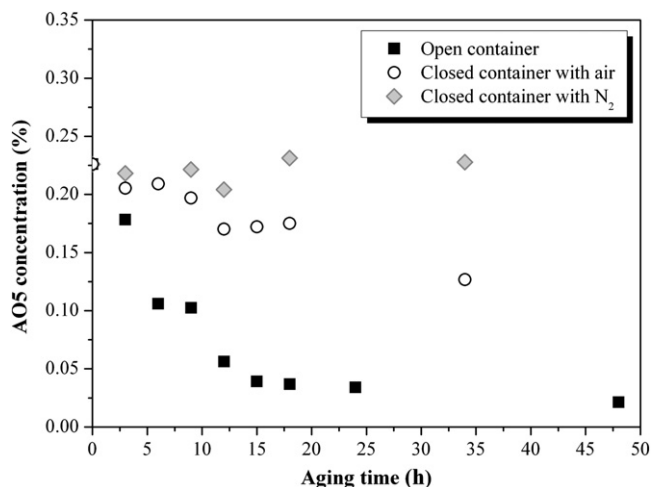


Fig. 1. Decrease of AO5 concentration versus time in an air-ventilated oven at 120 °C in an open container, a closed container under air and a closed container under nitrogen.

2. Equipment and experimental procedure

2.1. Materials

Commercial antioxidant 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) (AO5, $M_W = 340.5 \text{ g mol}^{-1}$, Ciba SC) and silicone oil DC 200 (Aldrich) with a viscosity at 25 °C of 50 mPa s were used.

2.2. Exposure conditions

The AO5 stabiliser was completely soluble in the silicone oil until 0.5% concentration. AO5 solutions in the silicone oil with a concentration of 0.2% in weight were prepared and exposed in an air-ventilated oven (at 120 °C and at atmospheric pressure) and in autoclaves at different temperatures (80, 90, 100, 110 and 120 °C) and at different oxygen pressures (0.2, 0.5, 1.0 and 3.0 MPa). Each experimental series was triplicated to evaluate the reproducibility.

The antioxidant evaporation loss was evaluated in an air-ventilated oven at 120 °C introducing the sample in three different environments: an open container, a closed container with air and another closed container with nitrogen. The thickness of liquid

samples was $\sim 1000 \mu\text{m}$. The stabiliser concentration change with aging time is shown in Fig. 1. Antioxidant concentration was measured by UV/VIS spectrophotometry. The antioxidant concentration of sample in the closed container with nitrogen remained constant during this test. However, the decrease of stabiliser concentration in the open container was higher than that contained in the closed container with air. This suggests that the concentration decay observed in the open container is mainly due to the antioxidant evaporation. Therefore, the study of stabiliser consumption by reaction with oxygen in air at atmospheric pressure was carried out in a closed container.

2.3. Analytical methods

The AO5 consumption and formation of reaction products were followed by UV/VIS spectrophotometry and by Gel Permeation Chromatography (GPC). A Perkin Elmer Lambda 35 UV/VIS spectrometer was employed to obtain the absorption spectra of the samples using cells of 500 μm optical path. GPC was performed using a system composed of a WATERS 714 plus autosampler chromatograph, a WATERS 484 tunable absorbance detector and a WATERS 2414 refractive index detector. Two serial columns 4.6 \times 300 mm were used: HR1 and HR4E. The measurements were done at 40 °C in tetrahydrofuran (THF) as mobile phase at 0.3 ml min^{-1} . The wavelength of the UV detector was fixed at 280 nm. About 70 mg of each sample in silicone oil were directly dissolved in 2 ml of THF. Dimethylphthalate was added as internal standard. 40 μl of obtained solution were injected into the column for analysis. Phenolic antioxidants with different molar masses were used as standards to evaluate the molar masses of oxidation products formed.

3. Results and discussion

3.1. UV/VIS analysis

Silicone oil solutions with increasing AO5 antioxidant concentration between 0.05 and 0.25% in weight were prepared and analysed by UV/VIS spectrophotometry to obtain the extinction coefficient. The molar extinction coefficient of AO5 in the UV was $4488 \text{ l mol}^{-1} \text{ cm}^{-1}$.

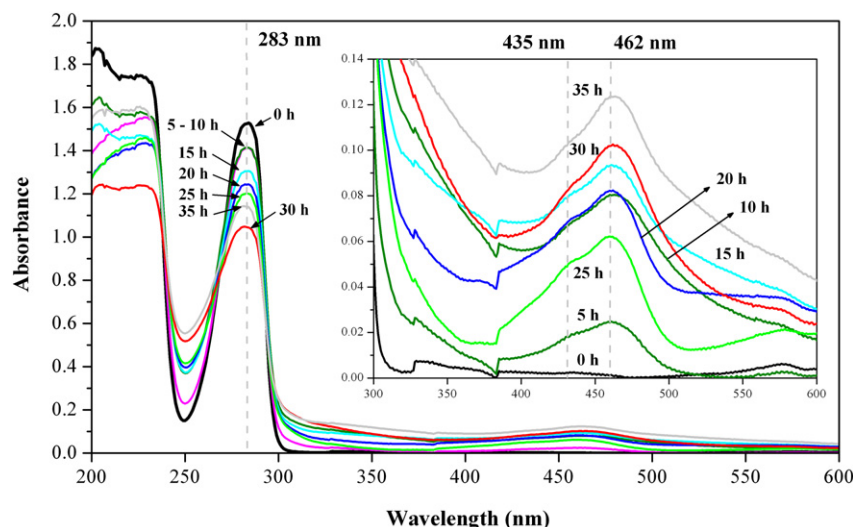


Fig. 2. Changes in the UV/VIS spectrum of AO5 sample as a function of the reaction time at 100 °C under 3.0 MPa oxygen pressure.

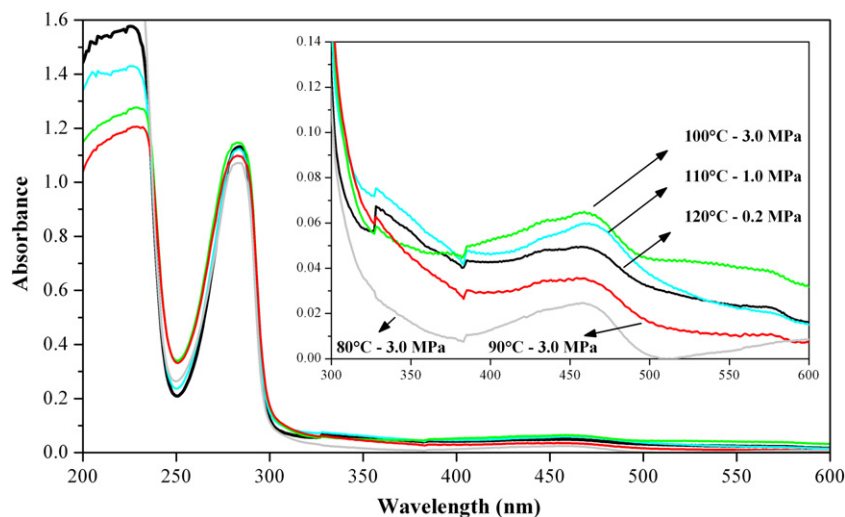


Fig. 3. UV/VIS spectra obtained at antioxidant fixed conversion ($[AO5]/[AO5]_0 = 0.75$) for different experimental conditions.

The changes in the UV/VIS spectra of AO5 solution as a function of the aging time at 100 °C under an oxygen pressure of 3.0 MPa are shown in Fig. 2. The spectrum of the unreacted AO5 antioxidant displays a single band at 283 nm. After 5 h exposure in these aging conditions, it can be observed a decrease of the band at 283 nm and the growth of a broad band in the visible region. This band displays a fine structure with a peak at 462 nm and a shoulder at 435 nm. The same trends were observed in the whole temperature/pressure/time range investigated. The changes were faster as temperature and oxygen pressure were higher. For a fixed degree of AO5 antioxidant conversion of 0.25, a similar UV/VIS spectrum was obtained independently of exposure conditions, as it is shown in Fig. 3. The fact that the absorbance of the oxidation products remained practically unchanged when varying the experimental conditions suggests that the mechanism could be the same.

The kinetic curves of antioxidant depletion at three different aging temperatures are shown in Fig. 4. A strong scatter of consumption data is obtained for the three experiments. This scatter makes the determination of a valid initial rate value of the antioxidant depletion difficult. The data scatter obtained by UV/VIS analysis must be due to the overlapping of the absorbance of the residual stabiliser band with the oxidation products formed.

3.2. GPC analysis

The GPC chromatograms related to the aging series of AO5 antioxidant at 100 °C under 3.0 MPa oxygen pressure are presented in Fig. 5. The molecular weight distribution corresponding to the unreacted stabiliser displays two peaks: AO5 antioxidant at a retention time of 22.5 min and the internal standard at 24.9 min. After oxidation, the antioxidant peak decreases and a broad band appears in the high molar mass range. It displays a fine structure with two clear maxima at 20.9 and 20.3 min, and a shoulder at 19.8 min. According to the calibration made with standard model compounds, these peaks would correspond to molar masses of $\sim 672 \text{ g mol}^{-1}$ (20.9 min), $\sim 953 \text{ g mol}^{-1}$ (20.3 min) and $\sim 1230 \text{ g mol}^{-1}$ (19.8 min). These molar masses correspond respectively, within experimental incertitude, to a dimer (681 g mol^{-1}), trimer (1022 g mol^{-1}) and tetramer (1362 g mol^{-1}) of the bisphenol under study. No lower mass products than original AO5 were observed.

The comparison between the results obtained by UV/VIS analysis and by GPC analysis is presented in Fig. 6, where the stabiliser consumption as a function of aging time at 90, 100 and 110 °C are

shown. The curves coincide, but UV/VIS results are considerably more scattered than GPC ones. In the following, GPC data will be used in the kinetic analysis.

3.3. Kinetic parameters

As it can be observed in the Fig. 6, the kinetic curves of antioxidant depletion seem to correspond to a simple apparent first order process, as expected for a single oxygen–phenol reaction if the oxygen concentration is maintained constant. The analytical investigations reveal the presence of a variety of by-products but apparently, they do not interfere with the oxygen–phenol reaction. In fact, Shanina et al. [5] proved that the initial consumption rate of AO5 in an inert substrate (chlorobenzene) and in a polypropylene matrix were practically identical, indicating that the initial consumption rate is predominantly controlled by reaction of phenol with oxygen. In the same way, Coquillat et al. [6] observed that the only way to explain the kinetic curve corresponding to the thermal oxidation of a phenol stabilised polybutadiene at 100 °C was considering the existence of this reaction. Therefore, the

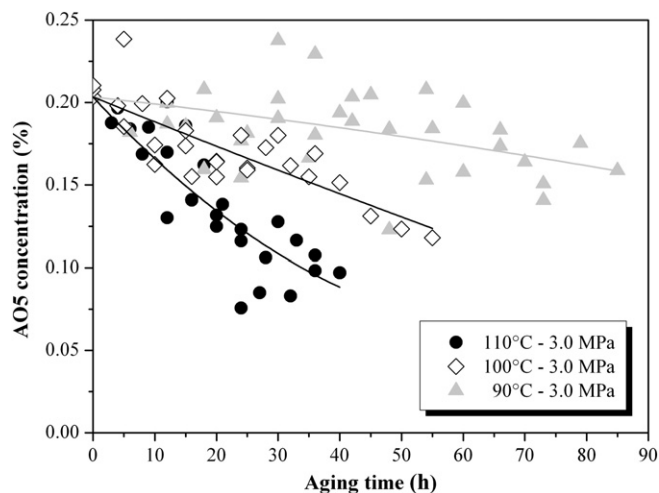


Fig. 4. Consumption of AO5 versus time obtained by UV/VIS spectrophotometry at three different experimental conditions (110 °C, 100 °C and 90 °C under 3.0 MPa oxygen pressure).

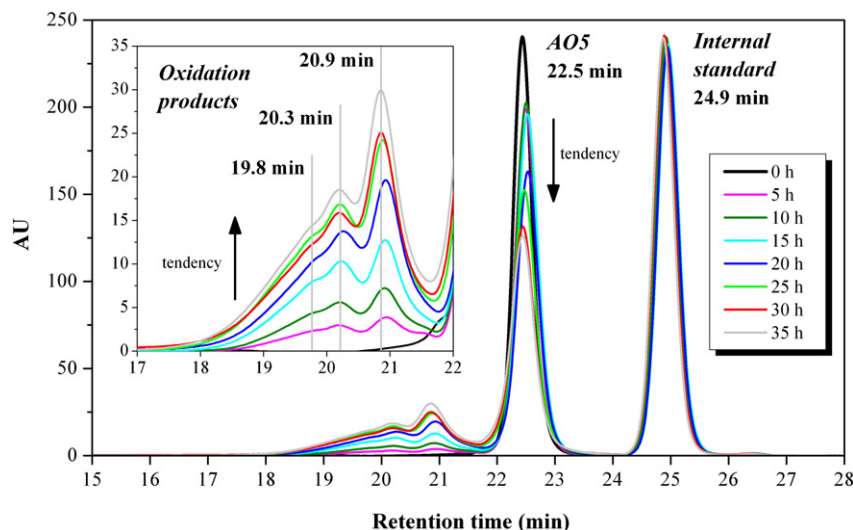


Fig. 5. Molecular weight changes of AO5 sample as a function of the reaction time at 100 °C under 3.0 MPa oxygen pressure.

oxygen rate constant can be estimated graphically from the stabiliser consumption rate.

$\text{AO5} + \text{O}_2 \rightarrow \text{oxidation products}$

$$r_{\text{AO5}} = r_{\text{O}_2} = -f_{\text{AO5}} k_{\text{O}_2} [\text{O}_2] [\text{AO5}]$$

where f_{AO5} is the phenol functionality ($f_{\text{AO5}} = 2$ for AO5), k_{O_2} is the true second order rate constant, $[\text{O}_2]$ and $[\text{AO5}]$ are the respective oxygen and residual stabiliser concentrations in the silicone solution. Here, $[\text{O}_2]$ is maintained constant so that the system behaves as a pseudo first order process.

$$\frac{d[\text{AO5}]}{dt} = -K[\text{AO5}]$$

where $K = 2 k_{\text{O}_2} [\text{O}_2]$. The integration leads to:

$$[\text{AO5}] = [\text{AO5}]_0 e^{-Kt}$$

K can be graphically determined from experimental results. Since f_{AO5} and $[\text{O}_2]$ are known, it is possible to determine the true second

order rate constant k_{O_2} . The oxygen concentration is the result of multiplying the oxygen solubility coefficient in the silicone oil ($\text{mol l}^{-1} \text{Pa}^{-1}$) by the oxygen pressure (Pa). The Clausius–Clapeyron equation was used to calculate the temperature dependence of the oxygen solubility [9].

Fig. 7 shows the first order plot obtained for the different experimental conditions. A good linear relationship is observed for all experimental conditions. The rate constant values are listed in Table 1. Another antioxidant concentration, ten times lower than the original concentration studied, was tested at 110 °C under 3.0 MPa. Similar kinetic parameters were obtained, indicating that the initial rate of antioxidant depletion is proportional to the initial antioxidant concentration. The same conclusion was achieved by Coquillat et al. [6]. The corresponding oxygen rate constants versus the inverse temperature in an Arrhenius plot are shown in Fig. 8. The Arrhenius plot shows a curvature, implying variations in the oxidation process mechanism with the temperature, which were not observed on chromatograms. If a linear approximation is taken, an activation energy of 112 kJ mol^{-1} is obtained. A similar value was obtained by Celina et al. [10] analyzing the AO5 depletion during the

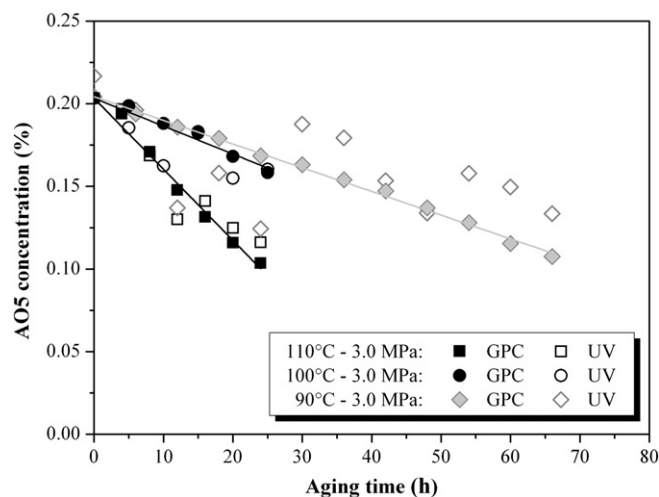


Fig. 6. Comparison of the consumption curves of AO5 versus aging time obtained by UV/VIS analysis and GPC analysis in three different experimental conditions (110 °C, 100 °C and 90 °C under 3.0 MPa oxygen pressure).

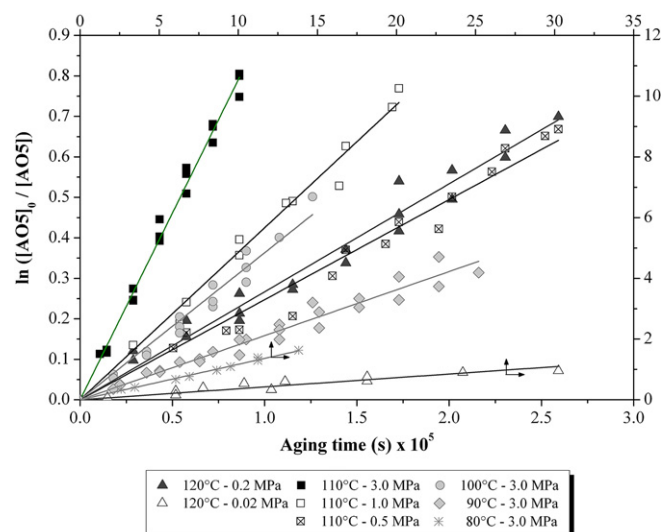


Fig. 7. First order plots in different experimental conditions.

Table 1
Kinetic parameters of the reaction of AO5 antioxidant with oxygen.

	T - P _{Oxygen}								
	80 °C 3.0 MPa	90 °C 3.2 MPa	100 °C 3.2 MPa	110 °C 0.5 MPa	110 °C 1.2 MPa	110 °C 3.2 MPa	110 °C 3.0 MPa ^a	120 °C 0.02 MPa	120 °C 0.2 MPa
K (s ⁻¹) × 10 ⁶	1.17	1.58	3.63	2.47	4.25	9.22	11.13	0.36	2.67
R ²	0.9948	0.9592	0.9710	0.9707	0.9854	0.9917	0.9922	0.9002	0.9680
k _{O₂} (l mol ⁻¹ s ⁻¹) × 10 ⁵	0.38	0.50	1.16	5.11	3.66	2.97	3.83	19.06	13.96

^a Concentration of 0.026% in weight.

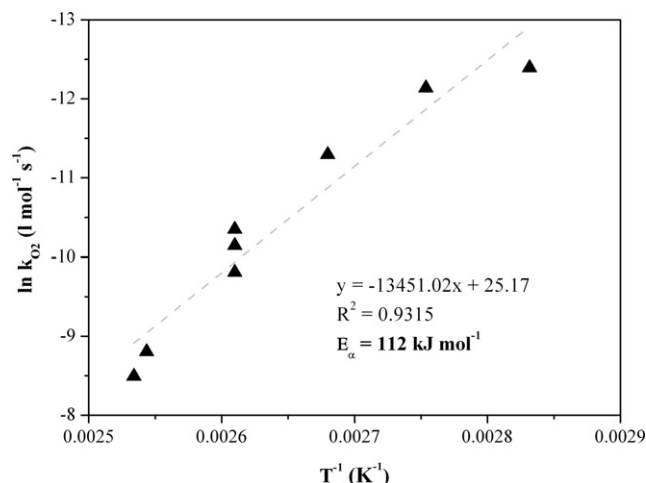


Fig. 8. Arrhenius plot of the k_{O_2} rate constants.

thermal degradation of a hydroxy-terminated polybutadiene from 50 °C to 110 °C (135 kJ mol⁻¹). However, a lower activation energy (48.1 kJ mol⁻¹) was calculated by Shanina et al. [11] with other methylene bisphenol antioxidant (2,2'-methylene-bis-[4-methyl-6-(1-methylcyclohexyl-1)-phenol]) in polyethylene–polypropylene blend matrices. These results suggest a strong influence of antioxidant structure in the aging process.

The true second order rate constants obtained in this work are compared with the values found by other authors in Fig. 9. The results obtained in this study fit with the values achieved by four different authors: Shlyapnikov et al. [7], Tyuleneva et al. [8], Shanina et al. [5] and Richaud et al. [12]. In their study, Shanina et al. [5] and Richaud et al. [12] used an inert molecular substrate, chlorobenzene, to analyze the consumption of phenolic antioxidants (AO5 by Shanina et al. [5] and Irganox 1010 by Richaud et al. [12]) in the thermal oxidation. Similar results were found when a polymer

matrix instead of an inert substrate was utilised. This is the case of Shlyapnikov et al. [7], who used a polyethylene matrix, and Tyuleneva et al. [8], who studied the kinetics of consumption of AO5 in polycarbonate. However, certain differences were appreciated with regard to the study made by Shanina et al. [11] in polyethylene–polypropylene blend matrices. These authors used another methylene bisphenol antioxidant different to AO5, 2,2'-methylene-bis-[4-methyl-6-(1-methylcyclohexyl-1)-phenol]. Apparently, the replacement of the tert-butyl group by a bulky group (the 1-methylcyclohexyl group) increases the antioxidant consumption rate during the process. On the other hand, different constant values were achieved by Coquillat et al. [6] and Celina et al. [10] when a polybutadiene matrix was used, although the global activation energy has a similar value to that found in our study.

3.4. Identification of oxidation products

Fig. 10 shows an example of the change of GPC chromatograms as a function of the retention time and the wavelength for an aged sample of AO5 (exposure conditions: 110 °C and 0.5 MPa during 78 h). The profiles corresponding to 282 and 467 nm are plotted in the front face of figure. The oxidation products are generated comprising the 17–22 min retention time range. This range corresponds approximately to molar masses ranging from 4900 to 380 g mol⁻¹, i.e. to degree of oligomerisation from 1 to approximately 14. Both AO5 antioxidant and oxidation products absorb at 282 nm, whereas at 467 nm only the oxidation products were detected. As it has been observed in the enlarged figure, three maxima at 20.9, 20.3 and 19.8 min, corresponding respectively to dimeric, trimeric and tetrameric quinone methides of AO5, reveal the existence of an oligomerisation process.

According to Pospíšil et al. [13,14] phenolic antioxidants undergo complex chemical transformations in the oxidation process and numerous transformation products are generated. The phenoxy radicals generated from the hydrogen abstraction in the

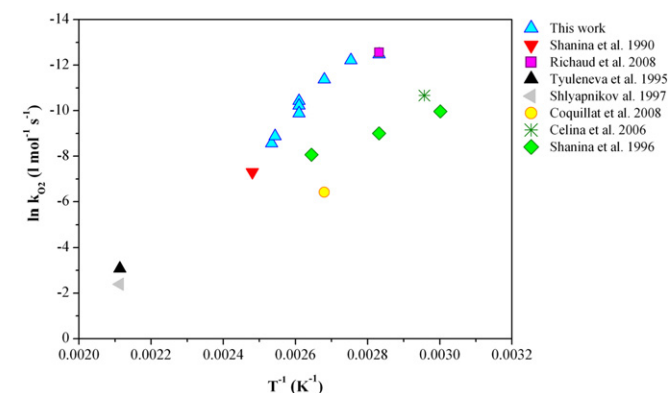


Fig. 9. Comparison in an Arrhenius plot of the true second order rate constants with literature data.

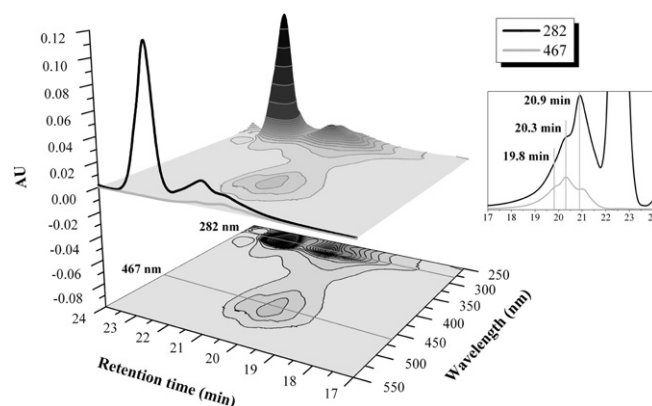
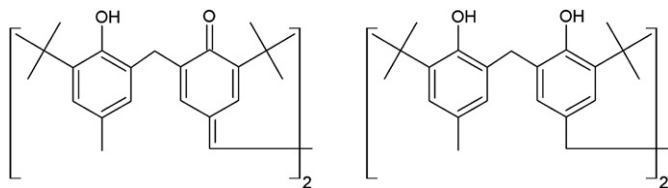


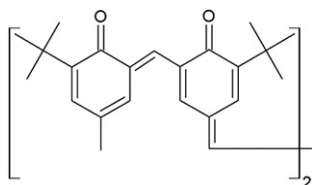
Fig. 10. Bidimensional and tridimensional plots illustrating the change of UV/VIS spectrum for the oxidation products of AO5 exposed at 110 °C under 0.5 MPa oxygen pressure during 78 h and separated by GPC.

antioxidant by oxygen are transformed via disproportionation into quinone methide structures. This process is improved by the presence of a hydrogen on the α -C atom at *para* position to the phenolic hydroxyl group [15–17]. Pospíšil et al. [14,15] detected structures similar to those showed in Scheme 1 and their analogous trimers and tetramers.



Scheme 1.

Yachigo et al. [16] also suggest the formation of structures like that shown in Scheme 2 as other probable compounds formed in the oxidation process of AO5.



Scheme 2.

Han et al. [18] also identified the dimer and trimer of AO5 during the thermal oxidation of polyethylene glycol at 80 °C in air. However, products with larger molecular weight than the trimer were not found.

The radicals generated could participate in other side reactions as C–C or C–O coupling involving C and O centred radicals, but in the case of AO5 these reactions are not very important, the formation of quinone methides being the major pathway [14]. The quinone-type molecules have been said to be responsible for the presence of coloured products. The quinone methides generated from the AO5 oxidation present a maximum absorption at 462–463 nm in the VIS region [15] observed as well in UV/VIS spectra as in GPC chromatograms. This absorption is responsible for colour appearance [16]. Many studies reveal that the quinonemethinoid moiety has no harmful effect on the efficiency of the attached phenolic moiety [13,19]. This fact could explain the consecutive formation of trimers and tetramers from the dimer.

4. Conclusions

The silicone oil matrix looks as an alternative inert substrate for study the oxidation kinetics of antioxidants with oxygen. Its presence does not interfere with the analysis techniques.

The AO5 consumption and the formation of reaction products were followed by two techniques, UV/VIS spectrophotometry and GPC, as a function of aging time. Similar results were obtained by both techniques. However, GPC permits separation of the residual antioxidant contribution from the formed reaction products, which leads to a lower data scatter than by UV/VIS.

Kinetic parameters of stabiliser consumption have been determined and compared with the values obtained both in inert and polymeric matrices by other authors.

In the analysis of the oxidation of formed products during the exposure process only oligomerisation compounds (dimers, trimers and tetramers) were observed.

The oxidation of hindered phenols is practically interesting for the following reasons:

- i) It has been observed in certain cases [5,6] that the consumption rate of antioxidants is maximum at the onset of exposure, while oxidation displays an induction period. This behaviour can be only explained by the direct oxygen–phenol reaction; this latter contributes to the antioxidant consumption and is responsible for a significant decrease of antioxidant efficiency.
- ii) In most cases, however, the oxygen–phenol reaction is negligible in usual exposure conditions. Nevertheless, in certain fields, for instance geotextiles [12], there is a tendency to accelerate aging by an increase of oxygen pressure to obtain results in reasonable times at relatively low temperatures (80 °C). Then, the reaction under consideration cannot be neglected.
- iii) One can reasonably expect that comparative studies of the oxidation of hindered phenols of different structures will bring a new insight on structure–reactivity relationship for this antioxidant family.

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